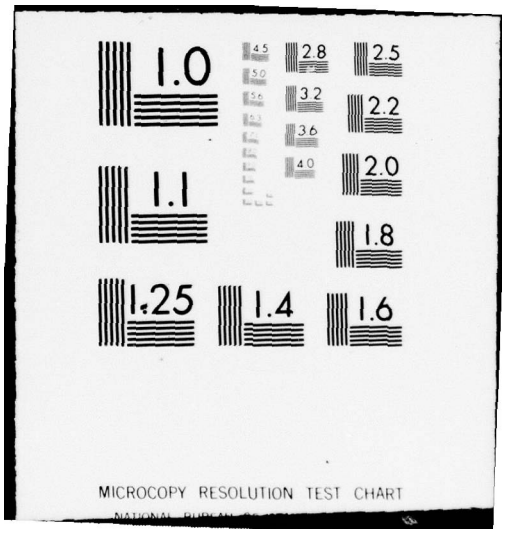
AD-A072 639 STATE UNIV OF NEW YORK AT ALBANY DEPT OF CHEMISTRY F/G 7/3
NUCLEOPHILIC SUBSTITUTION REACTIONS OF ALKYL, VINYL, AND ARYL
SEP 78 W D CLOSSON AFOSR-77-3241

UNCLASSIFIED AFOSR-TR-78-1448 NL

| OF |
ADA
072639

END
DATE
FILMED
9-79
DDC


1.0
1.1
1.25
1.4
1.6
1.8
2.0
2.2
2.5
2.8
3.2
3.6
4.0
4.5
5.0
5.6
6.3
MICROCOPY RESOLUTION TEST CHART

Unclassified

REPORT DOCUMENTATION PAGE

LEVEL II

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER: AFOSR-TR-78-1448	2. GOVT ACCESSION NO.
3. RECIPIENT'S CATALOG NUMBER	
4. TITLE (and Subtitle): Nucleophilic Substitution Reactions of Alkyl, Vinyl, and Aryl Trifluoromethanesulfonates	5. TYPE OF REPORT & PERIOD COVERED: Final Report. 1 Feb. 1977 — 31 July 1978
	6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s): William D. Closson	8. CONTRACT OR GRANT NUMBER(s): AFOSR-77-3241
9. PERFORMING ORGANIZATION NAME AND ADDRESS: Dept. of Chemistry, State University of New York at Albany, 1400 Washington Ave., Albany, N.Y. 12222	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS: 61102 F; 2303/B2
11. CONTROLLING OFFICE NAME AND ADDRESS: AF Office of Scientific Research/NC, Bolling AFB, D.C. 20332	12. REPORT DATE: September, 1978
	13. NUMBER OF PAGES: 24
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office): The Research Foundation of State University of New York, P. O. Box 9, Albany, N.Y. 12201	15. SECURITY CLASS. (of this report): UNCLASSIFIED
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

DDC RECEIVED AUG 13 1979 D

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Triflates, Triflamides, Aryl cations, Benzyne, Electron-Transfer, Sigma-n correlation, anion radicals, SRNI mechanism,

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The reaction of carbanion type nucleophiles with nitro substituted alkyl trifluoromethanesulfonate (triflate) esters has been shown to have very limited synthetic value. The usual result is formation of mixtures of tarry materials.

Reaction of aryl triflates with various nucleophiles appears to be limited to nucleophilic attack at sulfonyl sulfur and, for strongly basic, hindered, nucleophiles, generation of benzyne. Neither type of reaction offers significant synthetic utility.

(continued over)

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

403 448

20. (continued)

Electron-transfer (ET) reactions of several classes of trifluoromethanesulfonyl derivatives were examined. For alkyl and aryl esters, the chemistry is very similar to that of the corresponding methanesulfonate esters. Trifluoromethanesulfonamides, however, display a behavior uniquely different from that of all other sulfonamides. They undergo reductive cleavage (to amine and triflite ion) much more easily than do methanesulfonamides, they cleave via a pre-equilibrium electron-transfer mechanism, and the substituent effect upon their rates of cleavage correlates extremely well with σ^{-} constants.

Final Scientific Report

AFOSR Grant No. 77-3241A

"Nucleophilic Substitution Reactions of Alkyl, Vinyl, and Aryl Trifluoromethanesulfonates."

Principal Investigator: William D. Closson
Professor of Chemistry
State University of New York at Albany
Albany, New York 12222

Abstract

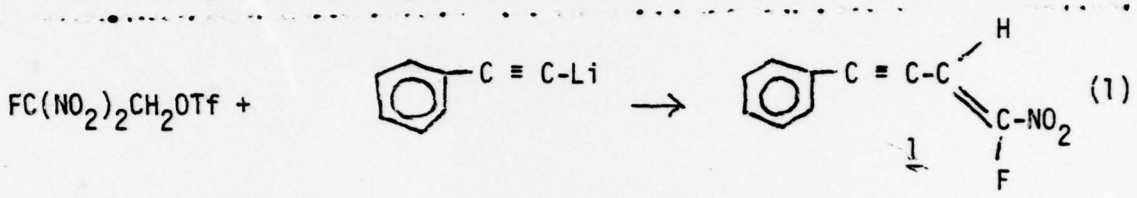
The reaction of carbanion type nucleophiles with nitro substituted alkyl trifluoromethanesulfonate (triflate) esters has been shown to have very limited synthetic value. The usual result is formation of mixtures of tarry materials.

Reaction of aryl triflates with various nucleophiles appears to be limited to nucleophilic attack at sulfonyl sulfur and, for strongly basic, hindered, nucleophiles, generation of benzyne. Neither type of reaction offers significant synthetic utility.

Electron-transfer (ET) reactions of several classes of trifluoromethanesulfonyl derivatives were examined. For alkyl and aryl esters, the chemistry is very similar to that of the corresponding methanesulfonate esters. Trifluoromethanesulfonamides, however, display a behavior uniquely different from that of all other sulfonamides. They undergo reductive cleavage (to amine and triflite ion) much more easily than do methanesulfonamides, they cleave via a pre-equilibrium electron-transfer mechanism, and the substituent effect upon their rates of cleavage correlates extremely well with σ^n constants.

I. Introduction

The main objectives of this research dealt with the unusual reaction between lithium phenylacetylide and 2-fluoro-2,2-dinitroethyl trifluoromethanesulfonate (triflate), shown in eq. 1, discovered by S. Shackelford at Seiler Research Laboratory. It was hoped to both determine the mechanism of this

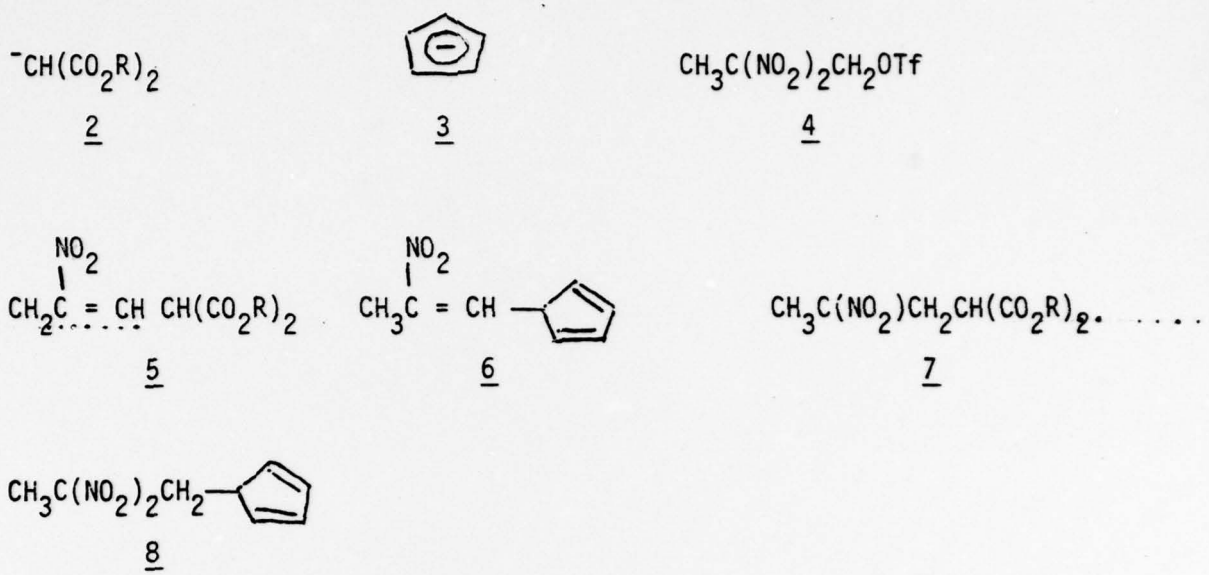


unusual transformation and also broaden its scope so as to extend it to triflate esters of other β-nitro alcohols and other lithium acetylide species. The reason this was felt to be important was that structures similar to 1, which would possess a conjugated enyne structure with attached fluoro and/or nitro groups but without the large, relatively inert phenyl group, would be promising materials for use as energetic binders, plasticizers, and crosslinking agents to replace nonenergetic materials currently used for these purposes. In addition, certain other classes of reactions of triflate esters and triflyl derivatives were to be explored, partly for their possible bearing on the mechanism of the reaction in eq. 1 and partly for their own intrinsic interest. These other areas and a brief rationale for their investigation are as follows:

a. Reaction of β-nitroalkyl triflate esters with other carbanionic nucleophiles.

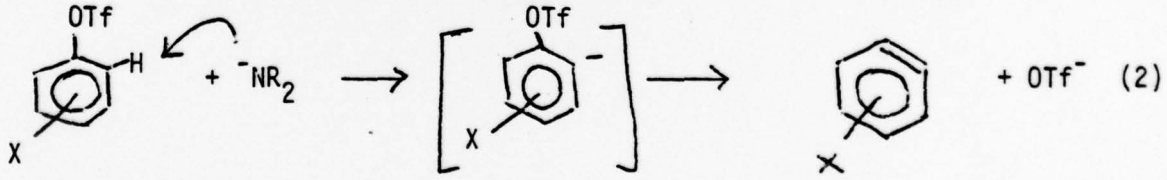
Reaction of carbanions such as malonate (2) and cyclopentadienide (3) with β-nitro triflate esters such as the dinitro propyl compound (4) might be expected to give either the nitro vinyl derivatives 5 and 6, in analogy with the reaction shown in eq. 1, or, possibly the direct substitution products 7 and 8. All of these materials would be of interest either as energetic compounds themselves or as precursors of other interesting materials:

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH (AFSC)
NOTICE OF TRANSMITTAL TO DDC
This technical report has been reviewed and is approved for public release IAW AFR 190-12 (7b).
Distribution is unlimited.
A. D. BLOSE
Technical Information Officer



b. Reaction of Aryl triflates with strong bases.

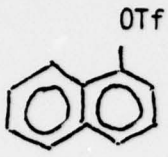
In analogy with some published work on reactions of other aryl sulfonate esters[1] one might expect production of benzyne (eq. 1). Considering the superiority of triflate over toluene- or benzenesulfonate (ca. 10^5-fold)[2] as a leaving group, and its greater inductive effect,[3] this might furnish a synthetically useful method for generating benzyne from phenol-type precursors.



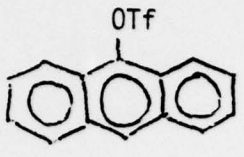
c. Possible SN1 reactions of aryl triflates.

Considerable interest has been exhibited over the years in the chemistry of phenyl cations but the only well-documented route to such species has been solvolysis of aryl diazonium ions.[4] Unfortunately, these species undergo numerous side reactions and interpretation of data from their reactions is often difficult. A few unsuccessful attempts at solvolysis of aryl triflates had been reported,[5] but we felt that polycyclic aryl triflates, such as 9 and 10, might

be more prone to ionize to triflate and aryl cations in polar solvents.



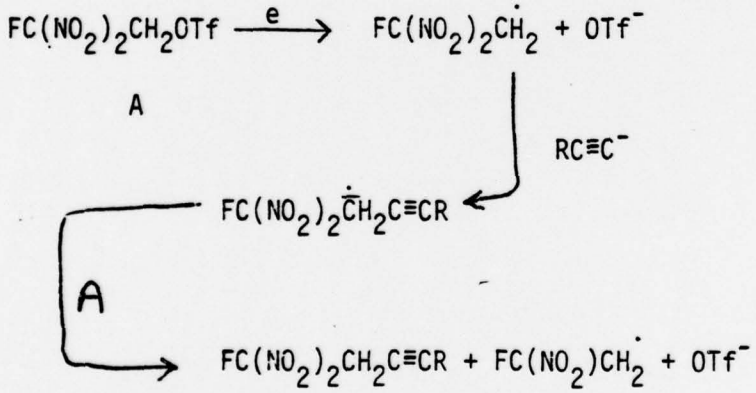
9



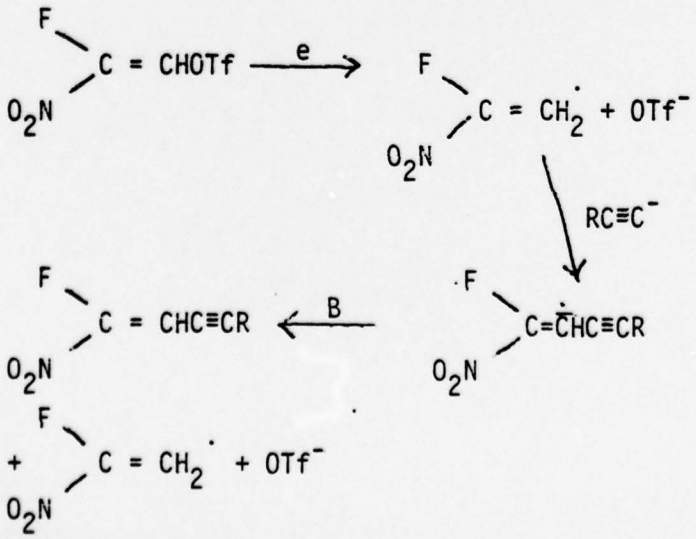
10

d. Reaction of triflate esters and other triflyl derivatives with electron donors.

This area of chemistry was felt to be important because formation of enyne 1 might be occurring by SRNI-type mechanisms[6] as indicated in eqs. 3 and 4. Also, since the electron-transfer chemistry of many sulfonyl systems is fairly well understood,[7] investigation of similar reactions of triflyl derivatives should yield interesting comparisons.



(3)



(4)

II. Results

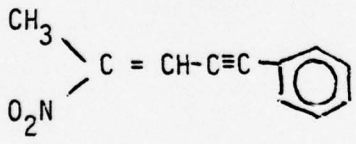
A. Determination of the mechanism of the enyne-forming reaction between lithium acetylides and β-nitroalkyl triflates.

Instead of examining directly the reaction between 2-fluoro-2,2-dinitroethyl triflate and lithium phenylacetylide we proposed to study reaction of the very similar 2,2-dinitropropyl compound (11) with the same nucleophile. The reasons for this choice were mainly ones of safety and practicality. Fluorodinitroethanol (12) is a very severe skin irritant[8] and is not readily available commercially. The dinitropropyl alcohol (13), on the other hand, is not as noxious and can be readily purchased from a number of companies. It can be converted to triflate 11 in quite good yield, and it was felt it should react readily with lithium phenylacetylide to yield enyne 14.

$CH_3C(NO_2)_2CH_2OTf$ — 11

$FC(NO_2)_2CH_2OH$ — 12

$CH_3C(NO_2)_2CH_2OH$ — 13



14

Unfortunately, we soon found that 11 cannot be converted to 14 as readily as 1 can be prepared from the fluorinated ester. In fact, in several dozen attempts in which a variety of solvents, temperatures, and modes of mixing reagents were examined, only once was a small yield (ca. 1%) of a compound that might have been 14 obtained. The amount was not sufficient even to allow identification of its structure. At about this stage of our work we learned that Shackelford and Druelinger at Seiler Research Laboratories had experienced similar difficulties with 11, and worse, had determined that about the only enyne-forming reaction that proceeded in reasonable yield with the fluorinated triflate was that shown in eq. 1, the originally discovered reaction.[9]

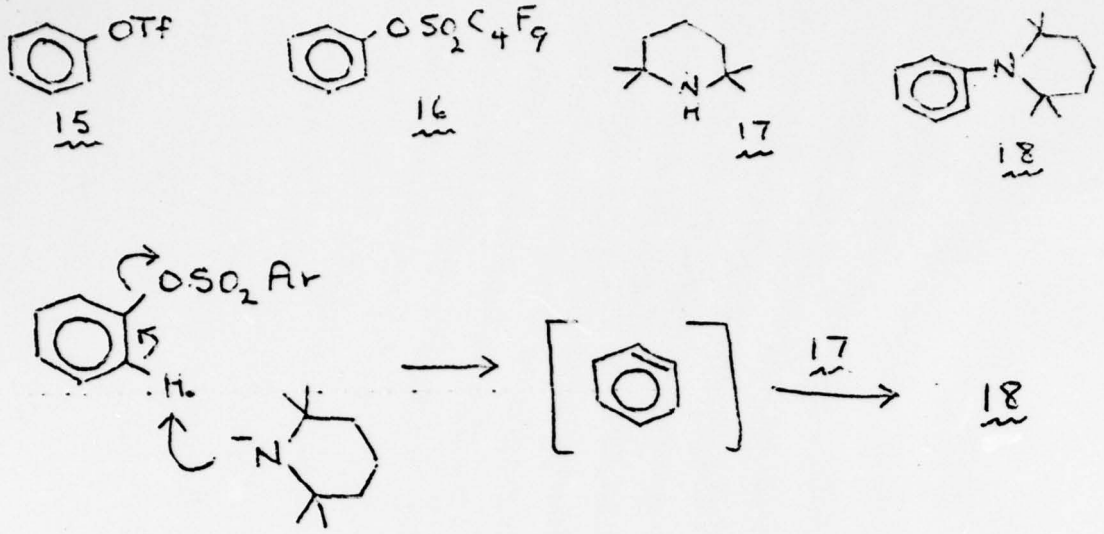
These developments were not only a major setback to our work, but also made determination of the mechanism of the enyne-forming reaction of questionable value. We were eventually able to secure a small supply of the fluoroalcohol 12 but by then other areas of research seemed more profitable to pursue. Our reasoning was that if the scope of the enyne-forming reaction is practically limited to formation of just one, not particularly useful, compound then knowledge of the reaction mechanism is not of pressing importance, either.

B. Reaction of β-nitroalkyl triflate esters with other carbanionic nucleophiles.

At the same time we were finding that reaction of 11 with lithium phenylacetylide failed to yield 14 (or anything else identifiable) we also found that 11 also failed to yield identifiable products on treatment with lithium salts of cyclopentadiene and diethyl malonate under similar conditions (diethyl ether solvent at ∿ -100°). The usual result was formation of a large number of tarry materials that would not separate on thin layer chromatograms. Reaction of 11 with cyanide ion also gave disappointing results. Several different procedures, employing THF or diethyl ether as solvents, different temperatures, and reaction times all gave about the same results.

C. Reaction of aryl triflates (and nonaflates) with strong bases.

The reactions of both phenyl triflate (15) and phenyl nonafluorobutanesulfonate (nonaflate) (16) with strong amide bases were examined, using conditions similar to those used by Fleming and Mah for conversion of phenyl benzenesulfonate to benzyne.[1] Reaction of both 15 and 16 with the lithium salt of 2,2,6,6-tetramethylpiperidine (17) in THF at 0° yielded modest amounts (ca. 20%) of the substitution product 18. Fleming and Mah reported a 40% yield of 18 in the reaction of either phenyl benzenesulfonate or toluenesulfonate with 17, and argued convincingly that it arose via formation of benzyne which then reacted with 17 or its anion (eq. 5).[1]



(5)

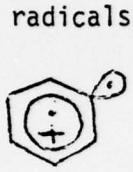
Unfortunately, attempts to improve the yield of benzyne derived products from 15 or 16, by way of longer reaction times, increased concentration of 17, or use of different solvents or bases, were unsuccessful. We conclude that while generation of benzyne from aryl triflates is feasible, it offers little advantage over the use of other, cheaper, aryl sulfonate esters.

D. Possible SN1 reactions of aryl triflates.

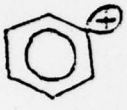
Shortly before our project started Hanack et al., published a long report on attempts at generation of aryl cations by solvolysis of aryl triflates and nonaflates.[10] Twelve different triflates and nonaflates were examined in great detail under a wide variety of conditions. In no case was heterolytic C-O cleavage observed. Either no reaction was observed, or nucleophilic attack at sulfonyl sulfur resulting in S-O cleavage was found. No evidence for production of aryl cations, even under the msot vigorous conditions (e.g., heating in water at 150° for 14 days), was obtained.

As noted in our proposal, however, Taft has proposed that the stable state of an aryl cation may be the triplet species 19 rather than the expected singlet structure 20,[11] and Symons and coworkers have recently demonstrated that photolysis of certain aryl diazonium salts at low temperature does yield meta-

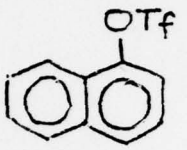
stable triplet species with structures presumably similar to 19.[12] We therefore felt that it was of importance to examine the reactions of some polycyclic aryl triflates, such as 21 and 22, since polycylic triplet species, such as 23, should be considerably more stable than monocyclic cations like 19, in analogy with the stability differences between polycyclic and monocyclic arene cation radicals.[13]



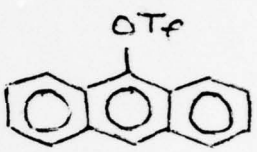
19



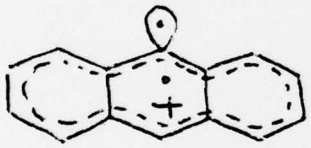
20



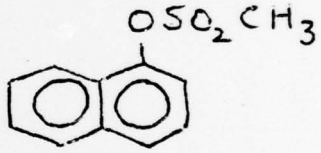
21



22



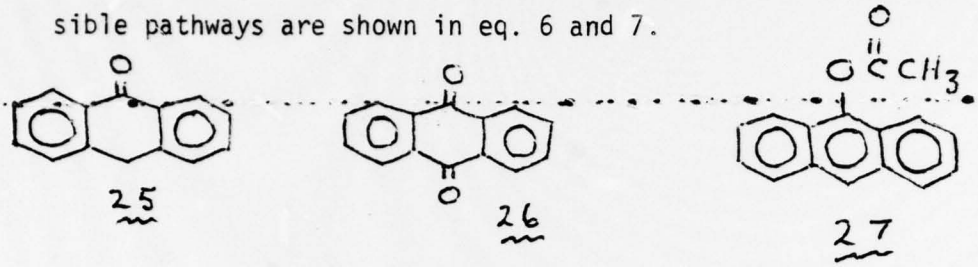
23



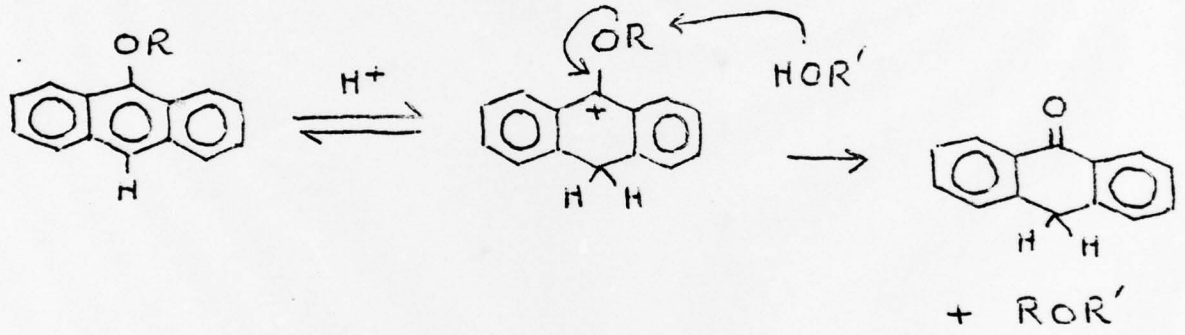
24

The 9-anthryl triflate (22) was easily synthesized and 1-naphthyl mesylate (24), a somewhat less reactive analog of 21, was available from some previous work. It was found that 22 underwent quite rapid reaction even under quite mild conditions (acetic acid solution, 98°, 10 hrs.), yielding a mixture of anthrone (25) and anthraquinone (26) on workup. (The formation of the quinone is probably due to autoxidation of anthrone during either the workup or during the reaction.) The reaction of 22 in several other solvent systems (e.g., trifluoroacetic acid, 2,2,2-trifluoroethanol, acetone-water) gave very similar results. It was also found that 9-anthryl acetate (27) rapidly yielded the same mixture of products in these solvents. The fact that the acetate, a derivative with an extremely poor leaving group, also shows about the same reactivity,

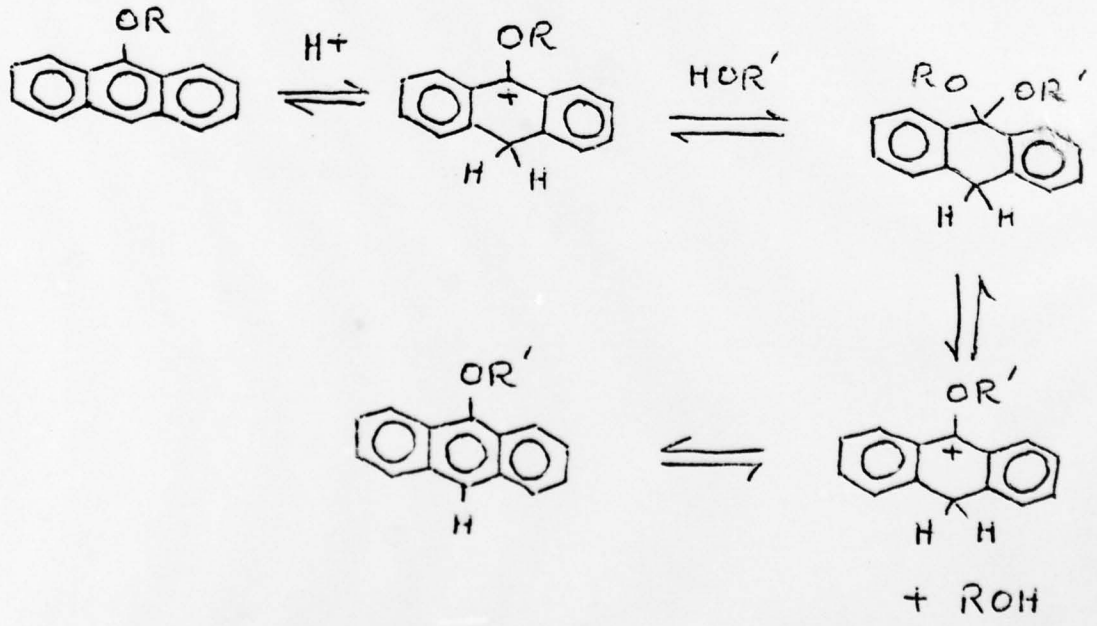
argues strongly against an SN1 type mechanism (heterolytic C-O cleavage) for these reactions. Most likely, some variant of the Bucherer reaction, an addition-elimination process, accounts for the unusual reactivity of 22 and 27. Two possible pathways are shown in eq. 6 and 7.



25 26 27



(5)



(7)

The naphthyl derivative (24) proved inert under all conditions tried, as did phenyl nonaflate.

E. Reaction of triflate esters and other triflyl derivatives with electron donors.

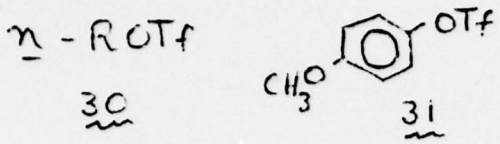
The initial impetus for this study was the concern that the enyne-forming reaction of 2-fluoro-2,2-dinitroethyl triflate might be occurring by an SRNI mechanism. For this radical chain process to occur, the triflate anion radical (28) must undergo C-O cleavage, yielding the species shown in eq. 8. If substitution occurs after elimination, then the vinyl ester anion radical (29) should

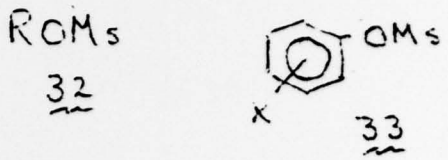
$$\underset{\underline{28}}{[FC(NO_2)_2CH_2OTf]^{\cdot -}} \longrightarrow FC(NO_2)_2CH_2^{\cdot} + OTf^- \qquad (8)$$

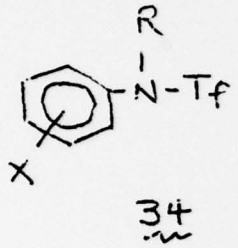
$$\left[\begin{array}{l} O_2N \\ \diagdown \\ \quad C = CHOTf \\ \diagup \\ F \end{array}\right]^{\cdot -} \longrightarrow \begin{array}{l} O_2N \\ \diagdown \\ \quad C = CH^{\cdot} \\ \diagup \\ F \end{array} + OTf^- \qquad (9)$$

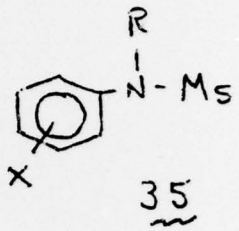
(29)

cleave as indicated in eq. 9. It was felt that electron-transfer reactions of the simple model compounds, n-hexyl and n-octyl triflate (30) and p-anisyl triflate (31) would be indicative of the behavior of 28 and 29. Study of these compounds would also avoid likely complications caused by the nitro groups in 28 and 29. Of further interest was the fact that the electron-transfer chemistry of alkyl (32)[7b] and aryl methane-sulfonates (33)[7c] had already been previously studied in our laboratory, and comparison of the chemistry of the fluorinated and nonfluorinated sulfonates would be interesting. Also, we decided to investigate the electron-transfer chemistry of the triflyl derivatives of substituted anilines (34) since we had carried out some unpublished work on the chemistry of the corresponding methanesulfonyl derivatives (35).

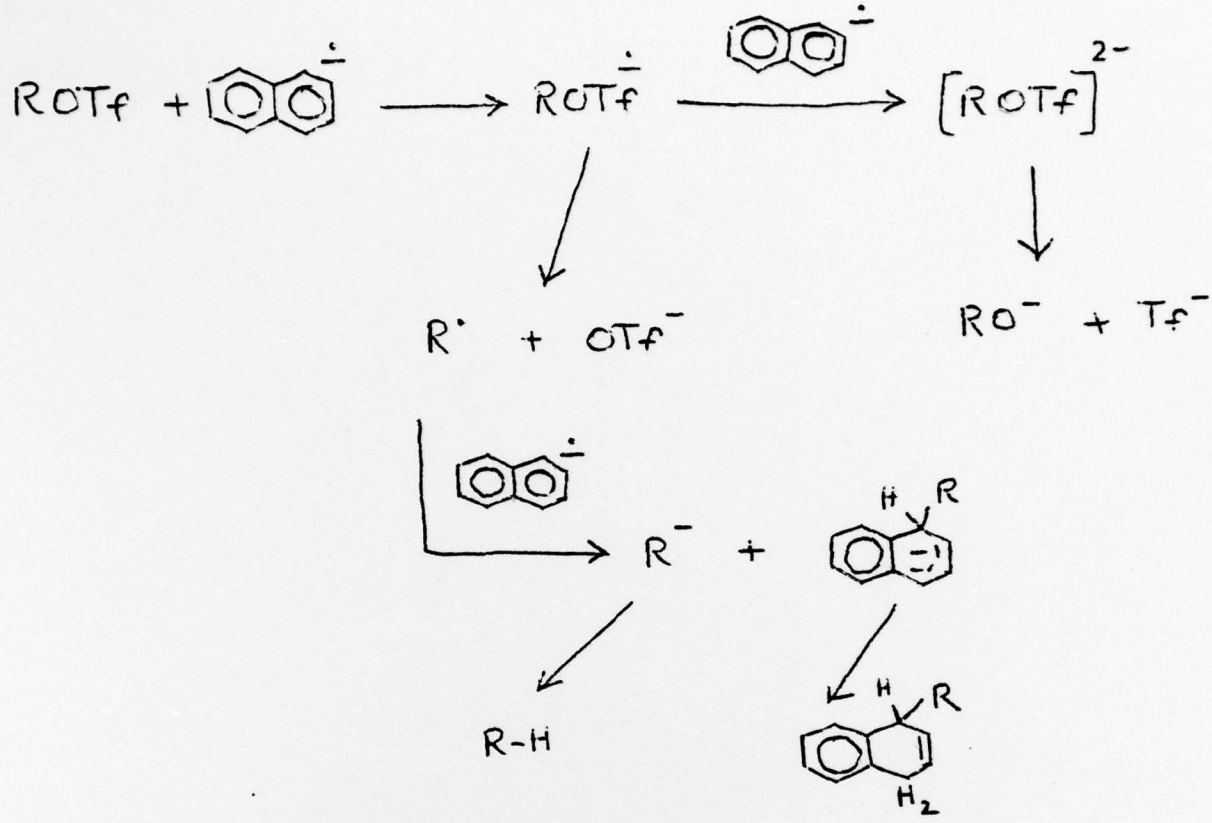






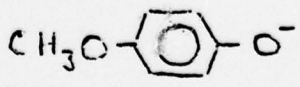


Treatment of the n-alkyl triflates (30) with sodium naphthalene, a powerful 1-electron reducing agent, in THF solution, yielded mixtures of n-alkanes, the corresponding alcohols, and alkylated dihydronaphthalenes. Attempts at obtaining quantitative measures of the yields of different products were not very successful due to the instability of the triflate esters. The nature of the product mixture, however, strongly suggests that they undergo reductive cleavage by the same mechanism as do the mesylate esters.[7b] This is outlined in eq. 10. Formation of alkylated dihydronaphthalenes and alkanes is particularly good evidence for intermediacy of alkyl radicals since it is well known that simple alkyl radicals yield almost equal amounts of coupling and reduction products on reaction with sodium naphthalene.[14] Formation of alcohol is most likely a result of further reduction of the triflate anion radical, as is known to be the case for alkyl methanesulfonates.[7b] In any case, the inferred C-O cleavage of the triflate anion radical would support the possibility of SRNI reactions for alkyl triflates.



(10)

The aryl triflate, 31, on treatment with either sodium naphthalene, or the weaker electron donor, sodium anthracene, gave only a quantitative yield of the corresponding phenoxide ion, 36. This is also quite similar to the previously observed behavior of the related aryl mesylates, 33,[7c] and tends to rule out the possibility of SRNI reactions for aryl and probably vinyl triflates. Formation of aryl radical in reaction of 31 should have yielded anisole under these conditions: none was found.

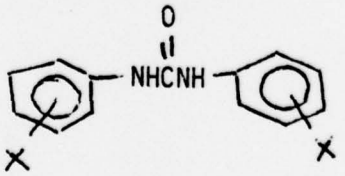


36

The electron transfer chemistry of the triflamides, 34, while not extremely relevant to the main thrust of our original proposal, turned out to yield the

most interesting results of all. That these results are of value is attested to by the fact the triflamido substituent, particularly when attached to an aryl ring, has a wide range of biological activity. Herbicidal,[15] anti-inflammatory,[16] and anticonvulsant activity[17] have all been reported. In addition, the triflamido group has enjoyed considerable synthetic use as an activating group and amino-protecting agent.[18] Additional knowledge of their chemistry is therefore likely to be useful.

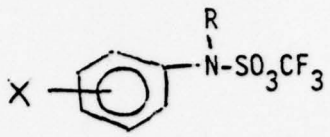
The series of different substituted triflamides, 34, listed in Table I was prepared by standard techniques. About the only interesting aspect of the syntheses was the formation of fairly large amounts of the corresponding ureas (37) during reaction of primary anilines and triflic anhydride. The urea-forming agent was traced to a volatile impurity present in the sulfonic anhydride. Whether this impurity was formed during conversion of trifluoromethanesulfonic acid to its anhydride on heating with phosphorus pentoxide, or was something initially present in the acid purchased from Aldrich Chemiical Co. could not be confirmed since all triflic anhydride prepared from sulfonic acid purchased since January of 1978 has failed to yield any urea. We can only assume that some impurity was present in the earlier batches of acid that either was converted to a urea-forming agent on treatment with P_2O_5, or was itself capable of yielding diaryl urea on reacting with primary anilines.



37

Table I

Properties of Triflamides



34

Substituents	m.p., °C	b.p., °C/mm Hz	Lit. m.p., °C
a, R=H, X=H	64-66		67[a]
b, R=H, X=p-CH_3	40-44		
c, R=H, X=p-CH_3O	36-37		38-41[b]
d, R=H, X=m-CH_3O	60-62		63-65[b]
e, R=H, X=p-Cl	47-49		50.5-51.5[b]
f, R=H, X=m-Cl	74-76		76-77[b]
g, R-CH_3, X=H		71/0.25	
h, R-CH_3, X=p-CH_3		83/0.75	
i, R=CH_3, X=p-CH_3O	35-36	115/0.80	
j, R=CH_3, X=m-CH_3O		105/0.60	
k, R=CH_3, X=p-Cl	30-31	102/1.0	
l, R=CH_3, X=m-Cl		109/0.95	
m, R=CH_3CH_2, X=H		73/0.50	

[a] J. B. Hendrickson and R. Bergeron, Tetrahedron Lett., 3839 (1973).

[b] J. E. Robertson, J. K. Harrington, and B. Mendel (Minnesota Mining and Manufacturing Co.) S. African 6804, 125, Nov. 14, 1968; Chem. Abstr., 71, 49571s (1967).

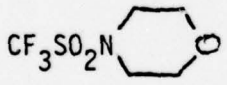
The overall reaction of triflanilides 34 with electron donors is rather similar to that of the corresponding mesylamides, 35. In short, the following statements can be made:

a. Triflanilides which do not possess an acidic hydrogen on nitrogen (34 g-m), are rapidly and quantitatively cleaved to amine anion and $CF_3SO_2^-$ by the anion radicals of naphthalene, phenanthrene, and anthracene in THF.

b. The stoichiometry of the reaction is 2 moles of anion radical to one mole of triflanilide.

c. Triflanilides possessing an acidic N-H group (34 a-g) are rapidly deprotonated by arene anion radicals, and the resulting salts are inert to cleavage.

d. Triflamides of purely aliphatic secondary amines, such as that derived from morpholine (38) are apparently not cleaved by any of the arene anion radicals tried (naphthalene, phenanthrene, anthracene).

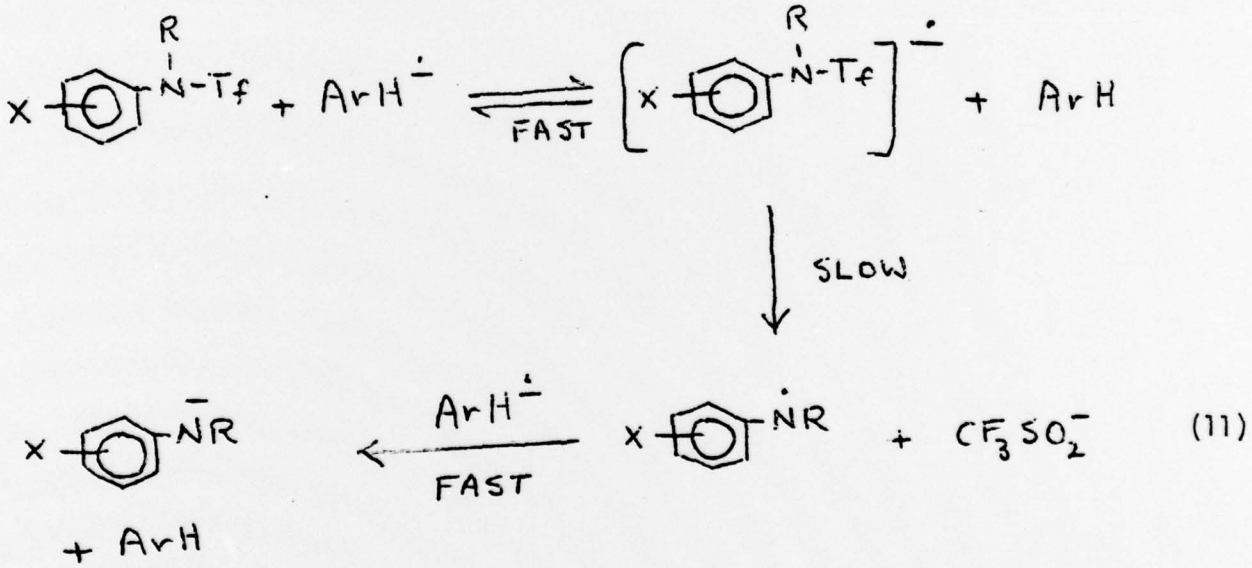


38

About the only major difference between mesylamides and triflamides is that weaker electron donors (such as sodium anthracene) are able to cleave the triflyl derivatives of N-substituted anilines but not the corresponding mesyl derivatives. This is not too surprising in view of the greater electronegativity of the triflyl group. A direct competition experiment between 34g and the corresponding mesylamide, using sodium naphthalene, showed the triflamide to be almost 19 times more reactive.

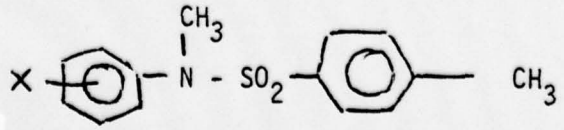
Further examination of the reactivity of triflamides, however, revealed some unique features. It was found that the relative rates of cleavage of dif-

ferent ring-substituted triflanilides were insensitive to the nature of the electron donor. Thus, the rate of cleavage of 34h was 0.5 times that of 34g with sodium anthracene ($E_{1/2}$ vs. SCE = -1.96V) and 0.47 with sodium phenanthrene ($E_{1/2}$ vs. SCE = -2.46V). This behavior is very similar to that of aryl methanesulfonates (33)[7c] and strongly implies a two-step, preequilibrium type of cleavage mechanism, as shown in eq. 11. This is quite different from the behavior of arenesulfonamides, whose relative rates are very sensitive to the nature of the electron donor, and which indicates that the rate-determining step is probably the initial electron transfer.[7a, 19]



(11)

Although the differences in cleavage mechanisms makes the comparison of somewhat doubtful value, direct competition measurements between triflanilides and corresponding toluene-sulfonamides 39, using sodium anthracene, showed the two classes of compounds to be almost of identical reactivities.



39

Similar comparison between 34g and phenyl methanesulfonate showed the phenol derivative to be ca. 75 times more reactive than the triflamide, with sodium anthracene as the electron donor.

Using sodium anthracene in THF and the competition experiment technique, the relative rates of cleavage of triflamides 34 g-l were determined. The data are given in Table II. Correlation of this rate data with σ-constants gave a very poor fit, r = 0.870. The correlation with σ° - constants was almost as bad, r = 0.890, but correlation with σ^n - constants was excellent, r = 0.995, ρ = + 3.74. In comparison, similar data for aryl mesylates correlated best with σ-constants, r = 0.987, ρ = + 3.00,[7c] and that for N-methyl-N-phenyl methanesulfonamides (using sodium naphthalene as the electron donor) also correlated best with σ-constants, r = 0.966, ρ = + 3.11.[20]

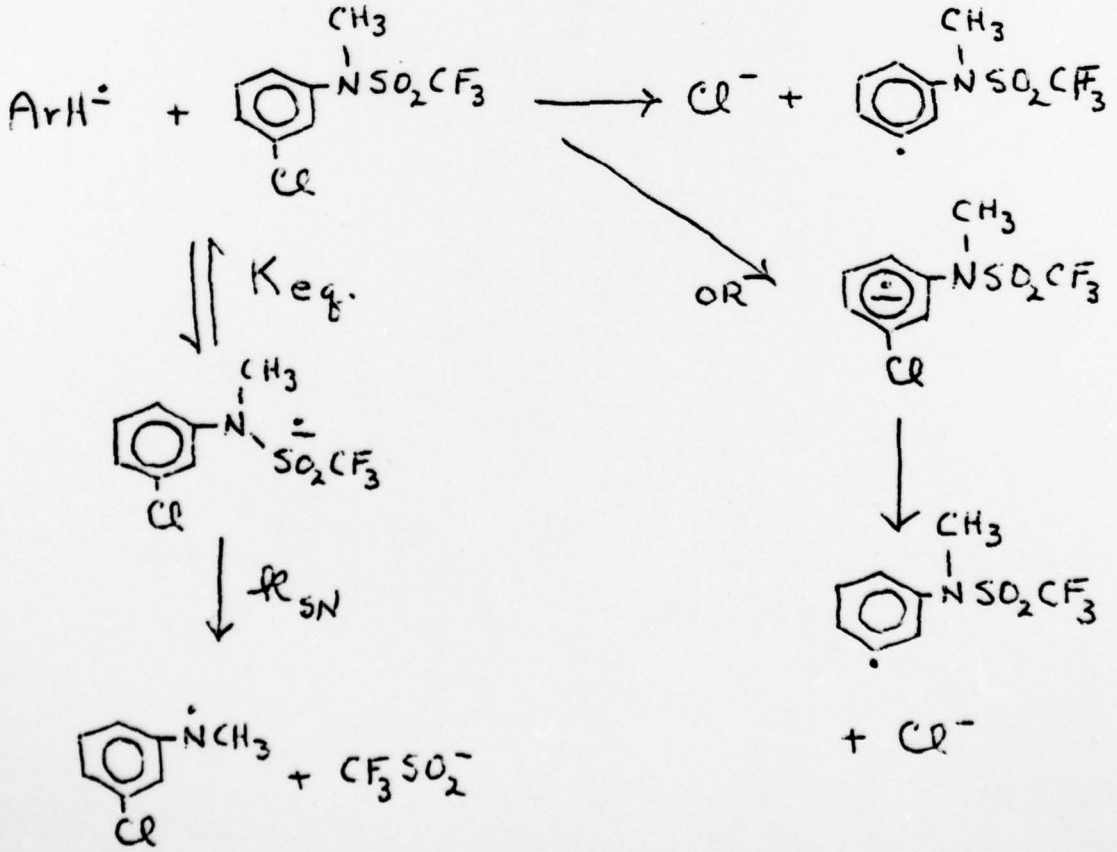
Table II

Relative Rate of Amine Formation in Sodium Anthracene Cleavage of Substituted N-Methyltriflanilides

Triflanilide	Substituent	Log Rel. Rate	σ	σ°	σ^n
34g	H	0	0	0	0
34h	p-CH_3	-0.3010	-0.170	-0.15	-0.129
34i	p-CH_3O	-0.3990	-0.268	-0.12	-0.111
34j	m-CH_3O	-0.1839	0.115	0.13	-0.076
34k	p-Cl	1.0310	0.227	0.27	0.238
34l	m-Cl	1.4239	0.373	0.35	0.373

Another interesting feature of the reductive cleavage of triflanilides was shown by carefully examining the products from reaction of the m-chloro compound, 34l, with sodium anthracene and sodium naphthalene. From reaction with anthracene anion radical, only m-chloro-N-methylaniline is obtained: dechlorination does not compete with S-N bond cleavage. On reaction with the more powerful electron

donor, naphthalene anion radical, both the m-chloroaniline and the dechlorinated triflamide, 34g, (ca. 15%) are obtained. The fact that the extent of C-Cl bond cleavage is different for different electron donors, while the relative rates of S-N cleavage stay the same argues that these two reactions follow entirely different pathways from the instant of the initial electron transfer. Once formation of the intermediate that must precede S-N cleavage has occurred (see eq. 11), dechlorination is no longer possible. One can reasonably argue that the triflamide anion radical that leads to S-N cleavage probably has the extra electron highly localized in the sulfonyl group, while C-Cl cleavage must either proceed via dissociative cleavage or prior formation of a different anion radical, possibly one with the extra electron localized in the aromatic ring. These possibilities are outlined in eq. 12. Similar reactions are displayed by ring-halogenated aryl methanesulfonates and have been rationalized in the same manner.[7c]



(12)

The correlation of the relative reactivities of the triflanilides with σ^n rather than with σ is quite interesting, but not easily explained. It is indicative of mainly an inductive interaction between the substituent and the site of reaction rather than a mixture of inductive and resonance effects that correlation with σ-constants would indicate. The relative rates of cleavage are a function of both an equilibrium constant (K_{eq}) and a rate constant (k_{S-N}) as shown in eq. 12. Since the k_{S-N} step might even have a negative reaction constant (reactions in which rather similar phenoxy radicals are generated often have negative ρ-values),[21] the equilibrium constant probably controls the value of ρ in this case. The poorer fit of the data with σ could be an indication that the strong inductive effect of the CF_3 group is the major stabilizing effect on the localized sulfonyl anion radical and that resonance effects from the substituent via the aryl ring and nitrogen are very minor. On the other hand, the large positive value of ρ(+ 3.74) indicates that inductive effects of these substituents, which must travel the same path, are considerable. Interestingly, Trepka, et al., observed a similar result when they examined the substituent effect on acidities of ring-substituted triflanilides.[15a] They found that the acidities correlated best with σ rather than with σ^-, as one might expect, yet the high value of ρ(+ 2.15) indicated considerable effect of the substituent.

In conclusion, triflamides are more readily cleaned by electron donors than are methanesulfonamides, but unlike arenesulfonamides,[7a] the reaction is limited to derivatives of aromatic amines. As a protecting agent for amino groups, simple benzenesulfonamides are superior. The mechanism of cleavage of triflamides, however, is unique among sulfonamides, and clearly reflects the large inductive effect of the CF_3 group.

Publication of the work dealing with the electron ➡ transfer chemistry of

triflamides is planned as soon as some minor aspects of the research are completed.

References

1. I. Fleming and T. Mah, J. Chem. Soc., Perkin I, 1577 (1976).
2. R. L. Hansen, J. Org. Chem., 30, 4322 (1965); A. Streitwieser, Jr., C. L. Wilkens, and E. Kiehlmann, J. Amer. Chem., Soc., 90, 1598 (1968); T. M. Su, W. F. Sliwinski, and P. von R. Schleyer, ibid., 91, 5386 (1969).
3. P. J. Stang and A. G. Anderson, J. Org. Chem., 41, 781 (1976).
4. C. G. Swain, J. E. Sheats, and K. G. Harbison, J. Am. Chem. Soc., 97, 783 (1975); G. G. Swain, J. E. Sheats, D. B. Gorenstein, and K. G. Harbison, ibid., 791 (1975).
5. A. Streitwieser, Jr., and A. Dafforn, Tetrahedron Lett., 1435 (1976); see also R. L. Hansen, U. S. Patent 3,346,612 (1967).
6. a. M. Kornblum, M. M. Kestner, S. D. Boyd, and L. C. Cattran, J. Am. Chem. Soc., 95, 3356 (1973), and subsequent papers.
   b. R. Rossi and J. F. Bunnett, J. Org. Chem., 37, 3570 (1972); J. K. Kim and J. F. Bunnett, J. Am. Chem. Soc., 92, 7463 (1970).
7. a. W. D. Closson, S. Ji, and S. Schulenberg, ibid, 92, 650 (1970).
   b. J. R. Ganson, S. Schulenberg, and W. D. Closson, Tetrahedron Lett., 4397 (1970).
   c. J. C. Carnahan, Jr., W. D. Closson, J. R. Ganson, D. A. Juckett, and K. S. Quaal, J. Amer. Chem. Soc., 98, 2526 (1976).
8. Personal experience of W. D. C.
9. Private communication from S. A. Shackelford, F. J. Seiler Research Laboratory, USAF Academy, Colorado 80840.
10. L. R. Subramanian, M. Hanack, L. W. K. Chang, M. A. Imhoff, P. von R. Schleyer, F. Effenburger, W. Kurtz, P. J. Stang, and P. E. Dueber, J. Org. Chem., 41, 4099 (1976).
11. R. W. Taft, J. Am. Chem. Soc., 83, 3350 (1961).

12. A. Cox, T. J. Kemp, D. R. Payne, M. C. R. Symons, D. M. Allen, and P. P. de Moira, J. Chem. Soc., Chem. Commun., 693 (1976).

13. G. Vincow, "Radical Ions," (E. T. Kaiser and L. Kevan, eds.), Interscience Publishers, New York, 1968, Chapt. 4.

14. J. F. Garst, Accounts Chem. Res., 4, 400 (1971).

15. (a) R. D. Trepka, J. K. Harrington, and J. W. Belisle, J. Org. Chem., 39, 1094 (1974);

(b) R. D. Trepka, J. K. Harrington, J. E. Robertson, and J. T. Waddington, J. Agr. Food Chem., 18, 1176 (1970);

(c) W. A. Gentner, Weed Sci., 21, 122 (1973).

16. G. G. I. Moore, "Antiinflammatory Agents," R. A. Scherrer and M. W. Whitehouse, Eds., Academic Press, New York, N.Y., 1974, Chapt. VI and references therein; G. G. I. Moore, J. K. Harrington, and K. F. Swingle, J. Med. Chem. 18, 386 (1975).

17. G. G. I. Moore, U. S. Patent 3,609,187 (1971); Chem. Abstr., 75, 151529D (1971).

18. J. B. Hendrickson and R. Bergeron, Tetrahedron Lett., 4607, 3839 (1973); ibid., 345 (1970).

19. K. Saboda Quaal, S. Ji, Y. M. Kim, W. D. Closson, and J. A. Zubieta, J. Org. Chem., 43, 1311 (1978).

20. P. Pierzchala, unpublished results, these laboratories.

21. M. A. DaRooge and L. R. Mahony, J. Org. Chem., 32, 1 (1967); J. C. McGowan, T. Powell, and R. Raw, J. Chem. Soc., 3103 (1959).